

~ Main results of the PhD Thesis ~

Preparation and investigation of multiphase High Entropy Alloys

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The concept of the thesis

In my doctoral thesis I would like to summarize my results regarding multiphase High Entropy Alloys (HEAs).

This new topic of materials science is dealing with metals in a completely different thinking than it was common for alloys so far. Whereas in the case of ordinary alloys, a mayor and some minor components in alloy were considered, the topic of HEAs deal with alloys containing many elements in equal or near equal atomic proportions. Thereby, the border between solute and solvent is blurred, in many cases indeterminable.

The name HEA originates from the concept, that high configuration entropy of many constituents can overcome the effect of enthalpy in the Gibbs-equiation, thus favor for solid solution phases over intermetallic ones. HEAs can be described as topologically ordered materials with chemical disorder, which serves as a basis for some special properties of these alloys, namely the sluggish diffusion, severe lattice distortion and cocktail effect. During my PhD work, the cocktail effect was investigated, so the influence of phase fractions and morphology on properties of HEAs. These properties are tunable with composition, annealing temperature and cooling conditions as well.

The Aims of this work

- Surveying the literature it turned out that although many composition families have been studied already, except the

Al, the systematic investigation of alloying with *sp* elements on a well known NiCoFeCr (called the stainless steel family) HEA was missing. This is why we decided to investigate the effect of other *sp* elements as Ge, Ge and Sn.

- On the other hand, our aim was to create a refractory type alloy, which contains Fe and is significantly cheaper than the existing 3d, 4d and 5d transition alloy based ones (like for example TiZrTaVNb). These high strength and high temperature refractory alloys, showing neutron irradiation resistance as well, are important, since they could be the possible structural materials of tomorrow.
- Preparing an alloy for Electron Back Scattered Diffraction (EBSD) is a challenging task even for a single phase material. In this work I have studied multiphase materials only, containing soft Face Centered Cubic (FCC) and hard Body Centered Cubic (BCC) phases. With this in mind, my aim was to create a recipe, what is reliable in the case of multiphase materials.

The selected alloy compositions which have been investigated in this work are presented in Table 1.

Applied methods

The investigated materials were prepared by myself in the Wigner Research Center for Physics, with induction melting. The samples were then investigated by X-Ray Diffraction (XRD),

NiCoFeCr based family
<i>Ni₂₀Co₂₀Fe₂₀Cr₂₀Al₂₀</i>
<i>Ni₂₀Co₂₀Fe₂₀Cr₂₀Ga₂₀</i>
<i>Ni₂₀Co₂₀Fe₂₀Cr₂₀Ge₂₀</i>
<i>Ni₂₀Co₂₀Fe₂₀Cr₂₀Sn₂₀</i>
Refractory type alloys
<i>Ni₂₀Fe₂₀Cr₂₀Mo₂₀W₂₀</i>
<i>Ni₃₅Fe₃₀Cr₂₀Mo₁₀W₅</i>

Table 1: Compositions investigated in this work

Scanning Electron Microscopy (SEM) and the standard mechanical investigation methods as hardness testing, tensile testing and compression of a micropillar. Phase information provided by XRD were double checked and even clarified with EBSD. The phase transformations were investigated with Differential Thermal Analysis (DTA).

Before each measurements, the sample's surfaces were prepared with standard metallographic methods.

Main results

TS1: It was found in all cases that the sp elements (X) are attached to Ni in the NiCoFeCr X system, where X means one of the four investigated sp element. This result is in strict connection with with enthalpy of forming. Furthermore, the chemical concentration distribution of the elements in the FCC/BCC phases generated after the doping, differ less in the case of Al containing sample (NiCoFeCrAl) and it is more accentuated for

the Ga, Ge, Sn elements [1].

TS2: Different FCC/BCC phase ratios were found even for the same VEC values of Al, Ga and Ge, Sn containing samples. This phenomena can be observed both on nanohardness measurements and the phase fractions measured by the SEM. Based on this, the electron affinity and/or the different enthalpies of forming between sp element and 3d partners should also be taken into account in the phase selection criteria [1].

TS3: It was also found that the initial paramagnetic NiCoFeCr alloy turned to be ferromagnetic by sp doping signalizing that at least one of the product phases is ferromagnetic at room temperature [1].

TS4: The doping of Ge to the NiCoFeCr system results on significant change in magnetic properties through obviously increased magnetic exchange parameters. Ge is BCC stabilizer in the NiCoFeCrGe system [2].

TS5: The NiCoFeCrGa alloy is metastable FCC+BCC duplex in as-cast state. Structural and chemical transformations can be performed on the system, which are sensitive to temperature and cooling rate as well [3].

TS6: In the case of 1100 K annealing ending with quick or medium cooling ($10^3 - 10^1$ K/s) the FCC/BCC ratio of the alloy

can be tuned without implying any changes in chemical homogeneity. This phenomena grants high mechanical tunability [3].

TS7: Near the Curie-point, the cube-like concentration fluctuations occur in the BCC phase of NiCoFeCrGa alloy. This phenomenon can be achieved by ~ 900 K annealing or higher temperature annealing, which end with slow cooling (10^{-1} K/s). This process is in clear connection with Cr migration and can be attributed to spinodal mechanism, since no grain boundary can be observed between parent grain and cubes [3].

TS8: The formation of cuboidal chemical segregation seems to be multistep, since two types of cubes are observable: „high Cr” and „low Cr” containing (see the Fig. 5.28). The Cr content of „high concentration cubes” is much above the concentration of the parent grain and the concentration of „low Cr content” cubes is near to the parent one.

TS9: The NiCoFeCrGa alloy possess an anomalous thermal expansion near to Curie point, which is attributed to its ferro- to paramagnetic transformation [4].

TS10: My results show unambiguous correlation between strength-ductility and phase composition of the NiFeCrMoW alloys. One can tune the phase fraction by adjusting the nominal composition and follow the brittle to ductile transition on these HEAs [5].

Conclusions

- We have shown the multiphas nature of *sp* element alloyed NiCoFeCr system, which result is in agreement with the Velence Electron Concentration (VEC) rule, widely applied in the literature. A reliable method was developed for a good quality sample preparation for EBSD measurements.
- We have shown a para to ferromagnetic transformation due to the precipitation of ferromagnetic BCC phase in the NiCoFeCrGe system.
- We have shown the metastable nature of NiCoFeCrGa as-cast alloy. With the help of targeted heat treatments we could change the phase fractions and morphology of the alloy, while the composition of FCC and BCC phases remained unchanged. Even chemical changes were found in the BCC phase of this alloy, which were in connection with Cr migration and a possible spinodal mechanism. The anomalous thermal expansion of NiCoFeCrGa was explained by the ferro to paramagnetic transformation at Curie point.
- In the case of NiFeCrMoW „refractory alloy” we have shown that phase ratios and morphology can be varied with nominal composition, thus the mechanical properties can be tuned. The heat tolerance and neutron irradiation tolerance investigations are in progress.

Author's related publications

- [1] Adam Vida, Lajos K Varga, Nguyen Quang Chinh, David Molnar, Shuo Huang, and Levente Vitos. “Effects of the sp element additions on the microstructure and mechanical properties of NiCoFeCr based high entropy alloys”. In: *Materials Science and Engineering: A* 669 (2016), pp. 14–19.
- [2] Shuo Huang, Ádám Vida, Dávid Molnár, Krisztina Kádas, Lajos Károly Varga, Erik Holmström, and Levente Vitos. “Phase stability and magnetic behavior of FeCrCoNiGe high-entropy alloy”. In: *Applied Physics Letters* 107.25 (2015), p. 251906.
- [3] Ádám Vida, Zsolt Maksa, Dávid Molnár, Shuo Huang, Jozef Kovac, Lajos K Varga, Levente Vitos, and Nguyen Q Chinh. “Evolution of the phase structure after different heat treatments in NiCoFeCrGa high entropy alloy”. In: *Journal of Alloys and Compounds* (2018).
- [4] Shuo Huang, Ádám Vida, Wei Li, Dávid Molnár, Se Kyun Kwon, Erik Holmström, Béla Varga, Lajos Károly Varga, and Levente Vitos. “Thermal expansion in FeCrCoNiGa high-entropy alloy from theory and experiment”. In: *Applied Physics Letters* 110.24 (2017), p. 241902.
- [5] Ádám Vida, Nguyen Q Chinh, János Lendvai, Anita Heczcel, and Lajos K Varga. “Microstructures and transition from brittle to ductile behavior of NiFeCrMoW High Entropy Alloys”. In: *Materials Letters* 195 (2017), pp. 14–17.